Determination of siderophile elements in metallic materials using multiple spot laser ablation-ICP-MS technique

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Abundances of siderophile elements in metallic phase of the meteorites can provide various cosmochemical information for the formation sequence of the core formation on the small planets including planetesimals[1]. Among the siderophile elements, fractionation pattern of Mo and W relative to other refractory siderophiles of similar volatility (Re, Os, Ir, Ru, Pt) reflects the oxygen fugacity or the partial pressure of oxygen in early solar system[2]. Despite this, sensitive and precise elemental analysis on metallic materials have been retarded mainly due to analytical difficulties, originating from low concentration of the elements and matrix effects.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has been used as a method to directly determine trace elemental composition in a metallic iron[3, 4]. With the LA-ICP-MS technique, multi-element determinations for trace-elements can be achieved. Moreover, with the newly developed multiple spot laser ablation protocol, elemental sensitivity and analysis repeatability can be further improved, and now the elemental determinations for trace-elements with concentrations of lower than ng g^{-1} can be made.

One of the major analytical difficulty to obtain reliable abundance data for analytes would be the availability of calibration standard with proper concentration ranges. This is the main reason why resulting abundance values for the trace-elements became erroneous. Faced with this, we have developed new analytical protocol using multi-spot laser ablation technique using a Galvanometric optics (msLA-ICP-MS). With the multiple spot ablation, two or more solid samples can be ablated almost at a same time, and the laser ablation induced sample aerosol could be mixed and introduced into the ICP-MS, suggesting that mixing, dilution of analytes, and spiking of second elements can be made just like a treatment of solution samples. This suggests that concentration ranges of the analytes can be adjusted, and therefore, the ranges of the calibration curve can be fit to the concentration range of the analytes.

In this study, present msLA-ICP-MS was applied for elemental determinations of 35 trace elements (B, C, Mg, Al, Si, P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Zr, Nb, Mo, Ru, Rh, Pd, Sn, Sb, La, Ce, Ta, W, Re, Os, Ir, Pt, Pb) in 13 various metallic materials (iron meteorite, low alloy steel, stainless steel, tool steel). Hence, concentration range for the analytes were adjusted by mixing two standard materials (JSS 654 stainless steel and Hoba IV iron meteorite). To evaluate the accuracy of the measurements, abundances of Cr in various materials were measured by the msLA-ICP-MS technique. The resulting abundance values for Cr was 7080±120 μg g^{-1} for NIST SRM 661 (low alloy steel), 15.78±0.41 % for JSS 650 (stainless steel), 23270±430 μg g^{-1} for JSS 603 (tool steel). These results exhibited good agreement with the literature values within 5 %. The detection limit calculated from the calibration curve is about 1 μg g^{-1}, thus the measurement with about 6 orders of magnitude in dynamic range could be made. The precision of the measurements defined by repeatability of the measurements from 5 times repeated analysis was better than 3 %. The precision and accuracy of the results obtained by the msLA-ICP-MS technique were comparable to those obtained by the solution based ICP-MS. In addition, similar accuracy and precision were obtained for other trace elements acquired simultaneously.

These data obtained here clearly demonstrate that msLA-ICP-MS can become a powerful tool for elemental analysis in solid samples. In this presentation, we will describe both the principle of msLA-ICP-MS and its application for the trace elemental analysis in metallic irons.

Reference
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